# Pilot scale application of a method for the analysis of perfluorinated compounds in surface soils

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## Abstract

A growing number of studies now indicate that perfluorinated compounds (PFCs) are globally distributed in the environment. Their widespread distribution and presence in remote locations has led to questions about the importance of atmospheric and oceanic transport, but describing their distribution in surface soils is also an essential but neglected element in developing a comprehensive understanding of their occurrence in the environment. Soils are the critical link between global atmospheric and hydrologic processes where both local and distant contaminants can accumulate and be released into aquatic and terrestrial communities. Because PFC concentrations in soils will influence ground and surface water, wildlife, and crops, methods to accurately measure PFCs in soil are clearly needed. To help answer this need, we developed a method for the analysis of nine perfluorinated carboxylic acids (C6 – C14) and four perfluorinated sulfonic acids (PFBS, PFHS, PFOS and PFDS) in soil. Samples from six nations (n = 10 per nation) were analyzed by LC-MS/MS to demonstrate the method performance parameters and to make preliminary observations about the occurrence of the PFCs in soils in different parts of the world. The resulting method shows acceptable performance characteristics for the target compounds in most soils and documenting the widespread occurrence of PFCs in surface soils. (*206 words)*



*Key words:* perfluorinated compounds, surface soils, PFOS, PFOA.


*Abbreviations:* PFCs, perfluorinated compounds; LC-MS/MS, Liquid chromatography tandem mass spectrometry;

## 1. Introduction

Perfluorinated compounds (PFCs) are a class of manmade chemicals that are now known to be globally distributed in environmental and biological media, with recent studies documenting their presence in surface water (Skutlarek et al., 2006; Nakayama et al., 2007; Konwick et al., 2008), air (Ellis et al., 2004; Stock et al., 2004; Stock et al., 2007), rainwater and snow (Kim and Kannan, 2007; Liu et al., 2009), and wastewater effluent (Schultz et al., 2006; Loganathan et al., 2007). They are also consistently found in blood serum of most people living in industrialized nations in the ng/mL range (Calafat et al., 2007), but the routes of exposure remain almost entirely undescribed. Possible sources of human exposure include drinking water (Emmett et al., 2006), food/food packaging (Begley et al., 2005; Tittlemier et al., 2007) and house dust (Strynar and Lindstrom, 2008), all of which have recently been shown to contain measurable levels of PFCs, but very little has been done to show how any potential sources relate to corresponding human body burdens. Moreover, transport and fate issues associated with this class of compounds remain poorly described. It is assumed that large quantities of these materials are maintained in atmospheric and oceanic pools, with weather and ocean currents being responsible for long distance transport, but the extent to which of these systems dominates has been a matter of debate, with limited data providing convincing evidence one way or the other (Ellis et al., 2004; Armitage et al., 2006). In short, PFCs are widespread, persistent, bio-accumulative, have demonstrated toxicity in laboratory animals, ecotoxicity and suggestive evidence of adverse effects on human health endpoints (Lau et al., 2007). Understanding the fate and transport of PFCs allows for a

75 better understanding of sources of human and ecological exposures and mitigation of
76 these exposures.
77
78 Considering the fact that roughly 30 % of the earth's surface is land,
79 approximately 150,000,000 $km^2$, it is surprising how little attention has been focused on
80 the role of soil in the transport and fate, transformation, and potential human exposure to
81 the PFCs. Given the large amount of PFCs thought to be in the atmosphere, and the fact
82 that PFCs are routinely measured in rain, snow, and dry deposition (Kim and Kannan,
83 2007), it is reasonable to hypothesize that this vast land surface will accumulate a
84 significant amount of PFC material. It is also reasonable to conclude that this material
85 will be important in terms of its movement and transformation in the environment, as
86 well as potential human exposures.
87
88 At present there are a few well documented cases of how soil can play a central
89 role in the environmental distribution and subsequent human exposure to PFCs. In what
90 has proven to be one of the most clear cut examples of how PFC- contaminated soils lead
91 to environmental disturbance and human exposure, Davis et al. (Davis et al., 2007)
92 documented a situation where over the course of 50 years, airborne emissions from a
93 fluoroploymer production facility in West Virginia were deposited in the soils of the
94 surrounding communities. Their study showed that ammonium perfluorooctanoate
95 (APFO) had accumulated in the soils above a municipal well field at concentrations
96 between 110-170 ng/g, with corresponding maximal concentrations in well water of
97 between 12,300–37,100 ng/L. Davis et al. concluded that APFO was transported via the

wind and deposited onto soils, and that subsequent rainfall caused the migration of perfluorooctanoate (PFOA) down through the soil into the groundwater. A study by Emmet et al. showed that people drinking this contaminated well water had circulating blood serum concentrations of PFOA that were approximately 100 times higher than the concentration in water they regularly consumed (Emmett et al., 2006). Together these studies clearly show how soils can be a site of deposition, long-term accumulation, and ultimately a significant source of human exposure to PFCs.

In another example of how contaminated soil can be a major factor in human exposure to the PFCs, Skutlarek et al. (Skutlarek et al., 2006) and Holzer et al. (Holzer et al., 2008) report on a situation in Germany where an "industrially contaminated" bio-solid material was inadvertently used as a soil amendment in a 10 hectare agricultural area. The situation was first discovered during a systematic survey of surface water quality on the Rhine River, where PFC concentrations were found to increase continuously up into the headwaters of the Möhne River valley. Ultimately, an adjacent agricultural area was found to be heavily contaminated with PFCs, with combined PFOS and PFOA levels reaching 6,300 ng/g soil. The surface water runoff from this area led to contamination of a drinking water reservoir, and because local water treatment processes were unable to remove the comparatively high levels of PFCs, individuals consuming this contaminated water had PFOA concentrations in their blood that were approximately 5 times higher than unexposed individuals from the same region (Holzer et al., 2008; Wilhelm et al., 2008a; Wilhelm et al., 2008b). These exposures to date have not been

linked to adverse human health outcomes as sufficient data does not yet exist to link acute and chronic exposure to PFCs with human health endpoints.

While the link between highly contaminated soils and human exposure is clear, the extent to which more typical soil concentrations influence human exposure remains unexplored. The aforementioned examples are extreme cases of soil PFC contamination relative to what is likely to be low to moderate ambient PFC soil concentrations. It is likely these low to moderate soil concentrations measured in this study will not be as significant a route of human exposure as more contaminated soil.

At present, relatively few studies have been devoted exclusively to the measurement of PFCs in surface soils (Washington et al., 2007). A basic standardized method with broad applicability would provide data that would be helpful for use in describing transport and fate issues, determining the impacts from local and remote sources, and for assessing potential human exposures. To meet these needs, we have developed a method for the detection and quantification of perfluorinated carboxylic acids (C6 – C14) and four perfluorinated sulfonic acids (PFBS, PFHS, PFOS and PFDS) in surface soils (Table 1). Its utility is evaluated with the analysis of soil samples collected from various locations around the world. The samples were chosen to represent "background" PFC contaminated soils, avoiding samples with known PFC contamination. The performance of the method and the implications of the findings relative to global distribution of the PFCs are considered below.

## 2. Materials and methods

## 2.1 Chemicals

Potassium salt of perfluorobutane sulfonate (PFBS, 98%) was provided by 3M Company (St. Paul, MN, USA). Potassium salts of PFOS (98%) and perfluorohexane sulfonate (PFHS 98%) and perfluorohexanoic acid (C6, 97%) were purchased from Fluka (Buchs, Switzerland). Sodium salt of perfluorodecane sulfonate (PFDS, 98%) was purchased from Wellington Laboratories (Guelph, Ontario, Canada). Perfluoroheptanoic acid (C7, 99%), C8/PFOA (96%), perfluorononanoic acid (C9, 97%), perfluorodecanoic acid (C10, 98%), perfluorotridecanoic acid (C13, 97%) and perfluorotetradecanoic acid (C14, 97%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Perfluoroundecanoic acid (C11, 96%) and perfluorododecanoic acid (C12, 96%) were purchased from Oakwood Products (West Columbia, SC, USA). Five internal standards were used for the analysis: $^{18}O_2$-Ammonium perfluorooctane sulfonate ($^{18}O_2$-PFOS) was purchased from Research Triangle Institute (Research Triangle Park, NC, USA);1,2-$^{13}C_2$-labeled PFOA ($^{13}$C-PFOA) was purchased from Perkin-Elmer Life and Analytical Sciences (Boston, MA, USA); $^{18}O_2$-PFHS, $^{13}C_2$-C11 and $^{13}C_2$-C6 were purchased from Wellington Laboratories (Guelph, Ontario, Canada). All target compounds, internal standards, and their abbreviations are listed in Table S1. Methanol (B&J Brand High Purity Solvent) was purchased from Honeywell Burdick & Jackson (Muskegon, MI, USA) and ammonium acetate from Sigma Aldrich (St. Louis, MO, USA). Deionized water was generated in house from a Barnsted Easypure UV/UF (Dubuque, IA, USA) coupled with activated charcoal and ion exchange resin canisters.

## 2.2 Preparation of standard solutions

Individual stock solutions of the PFCs were made by dissolving 100 mg analyte in 10 mL of methanol for a nominal concentration of 10,000 ng/μL. The exceptions were for C13 and C14 compounds, which were dissolved in ethanol due to limited solubility in methanol, and PFDS, which was purchased as a methanolic solution. Perfluorinated sulfonic acids (PFBS, PFHS and PFOS) were adjusted for $K^+$ ion content so the resulting perfluorinated anion was ~ 100 mg per 10 mL methanol. Stock solutions were stored on the bench-top at ambient temperatures in glass vials with foil lined caps. Working solutions were made by combining all PFC stock solutions together and dilution to a concentration of 100 ng/μL methanol. Serial dilutions of the primary working solution were made in BD Biosciences 15 mL polypropylene Falcon tubes (San Jose, CA, USA) to cover the working range of the standard curves.

**2.3 Soil Collection and Processing**

All samples discussed in this document were obtained under the terms of a soil collection and storage permit issued by the US Department of Agriculture (# S-75871) which specifies how samples from various origins must be shipped, stored, and disposed of in order to prevent the spread of potentially invasive species and pathogens. Sixty soils, representing 10 samples from each nation, were randomly selected from over 300 fresh and archived surface soils samples that were sent to the analytical lab by various collaborators in United States, China, Japan, Norway, Greece, and Mexico in 2007. These soils were selected to represent a wide range of chemical and physical characteristics for evaluation during this method development process. Care was taken to exclude soils from areas with known PFC contamination and/or in the vicinity of

industries known to use PFCs. These soils were not intended to be representative of the nation of origin, but they considered to be useful as indicators of background concentrations in different soil types and parts of the world.

Fresh samples were acquired (n = 237) from A-horizon surface soils using a stainless steel trowel pre-cleaned with methanol (2x). Soil was collected as a composite sample from multiple locations within a 1 $m^2$ area at 0 – 15 cm depth and aggregated into one storage container. Approximately 200 – 500 grams of fresh soil was shipped in commercially available polyethylene zip-top bags. The soil sample location (GPS coordinates if available) was noted, and the sample was labeled with a unique identification number and a date. At the analytical laboratory samples were stored at 4°C until analysis. Archived soil samples (n = 100) were likewise shipped in commercially available polyethylene bags, with no further treatment. All soil samples were sieved at original moisture content upon receipt through a cleaned brass or stainless steel #10 mesh sieve (2 mm) by mechanical shaking. Soil passing the 2mm sieve was stored in the original container or in an appropriate commercially available polypropylene bag that was verified to be free of perfluorinated compounds. Material not passing through the sieve was discarded. Samples that were too moist for sieving were allowed to air dry for an appropriate time until sieving was physically possible. Between samples the sieving apparatus was washed with a bristle brush and mild detergent to remove all soil particles, rinsed thoroughly with tap water, rinsed with DI water (2x), and then methanol (1x) before drying for further use.

All soil samples were analyzed at moisture content after sieving and storage. To normalize data sub-samples (2-3 g) of all 60 samples were weighed, placed in a drying

oven for 24 hrs (105°C), and then re-weighed to calculate the original moisture content so that all results discussed below could be reported on a ng/g dry weigh basis.

**2.4 Soil Extraction and Cleanup**

For each sample (unknown, replicate, or spike), the storage bag was rotated in the x, y and z plane for 1 minute, after which approximately 2 grams was removed for analysis. The soil sample was placed in a clean BD Biosciences 15 mL polypropylene Falcon tube (San Jose, CA, USA) and 10 mL of methanol containing 10 ng of each of the 5 perfluorinated internal standards (IS) was added to each tube. Samples were shaken for 30 minutes, sonicated in a water bath for 30 minutes, and centrifuged at 16,800 g for 5 minutes. The methanolic supernatant was removed with a Pasteur pipette and subjected to solid phase extraction (SPE) cleanup using Supelco Supelclean ENVI-Carb 3 cc (0.25 g graphitized carbon) cartridges (Supelco, Belefonte, PA, USA). SPE cartridges were placed in a vacuum manifold and pre-conditioned with 5 mL of methanol (2x). Eluates were collected in a clean 15 mL B&D Falcon polypropylene tube and concentrated to 2mL under nitrogen at 50°C using a Zymark TurboVap LV (Caliper Life Science, Hopkinton, MA, USA). A subsample of the reduced extract was mixed 50:50 (v/v) with 2 mM ammonium acetate for UPLC/MS-MS analysis.

**2.5 Chromatographic and mass spectrometer conditions**

Analysis was performed using a Waters Acquity™ ultra performance liquid chromatograph interfaced with a Waters Quattro Premier XE triple quadrupole mass spectrometer (UPLC-MS/MS) (Waters, Milford, MA, USA). A 40 μL aliquot of the

sample was injected onto an Acquity UPLC® BEH C18 column (2.1 mm i.d. × 50 mm, 1.7 μm; Waters, Milford, MA, USA). The mobile phase was made up of 2 mM ammonium acetate aqueous solution with 5% methanol (solvent A) and 2 mM ammonium acetate in methanol (solvent B). The UPLC run consisted of a gradient, starting with 60% solvent A at a constant flow rate of 0.5 mL/min. The gradient was increased to 90% solvent B at 3.5 min and 100% solvent B at 3.6 min and held for 0.9 min. At 4.6 min the gradient was returned to the original conditions and held until 6.0 min. A holdup column (Waters corporation PFOS/PFOA holdup column 2.1 x 50 mm prototype Milford, MA, USA) was installed between the aqueous side pump and the mixing chamber to eliminate contamination resulting from buildup of PFCs from the mobile phase on the head of the LC column during column equilibration. Electrospray negative ionization was used in the mass spectrometer source**.** The capillary voltage was set at negative 0.4 kV. Cone gas and desolvation gas flows were 0 and 1200 L/h, respectively. The source temperature was 150ºC and the desolvation temperature was 350ºC. Transitions for all ions were observed using multiple reaction monitoring (MRM) and analyte-specific mass spectrometer parameters were optimized for each compound. One primary transition was used for quantitation, and the ratio of the primary transition ion to a secondary ion was used for confirmation (Table 1).

**2.6 Quantitation**

Considering the broad range of chemical and physical characteristics in all of the different soils under investigation, and the fact that no suitable blank matrix could be identified for construction of matrix matched curves, solvent-based calibration curves

were used for quantitation. Six point calibration curves containing native standards and IS were prepared in a range from 0.5 to 50 ng/g dry weight for each analyte. The ratio of the analyte peak area to the IS peak area was plotted against concentration and fitted with a quadratic regression using 1/x weighting. All curves had a coefficient of determination ($r^2$) of 0.99 or greater with the limit of quantitation (LOQ) being defined as the lowest point on the curve that back predicted within ± 30% of the theoretical value. All other points were within ± 20% of their theoretical concentrations. Quanlynx software (version 4.1, Waters Corporation, Milford, MA) was used for sample quantitation.

**2.7 Quality control**

In preliminary range finding analyses, 10 soils with measureable levels of the PFCs were identified for use as quality control (QC) material. These soils were combined and thoroughly mixed to create a composite bulk QC pool with naturally occurring levels of each PFC. In each analytical batch, two replicate samples of this QC pool were analyzed along with the unknown samples (n = 20). Analytical runs were deemed to be acceptable if the concentration of the analytes in the QC soils were within ± 20% agreement of the average concentration determined for each compound. A total of eight replicate analyses over four analytical batches were used to generate target QC values. Moreover, the precision of the method was determined by calculating the average coefficient of variation (CV) of the replicate analysis of QC pool material.

As an additional measure of method precision, 10% of all unknown samples were randomly selected for replicate analysis (n = 6). As a measure of percent recovery, 10% of the samples were reanalyzed after spiking with 50 ng (50 uL of a 1 ng/uL standard

281 solution) of each target analyte. Percent recovery was subsequently determined by
282 subtracting predetermined endogenous levels from the spiked soils, and comparing the
283 observed increase to the theoretical amount added (50 ng). Quantitation/confirmation
284 ion ratios were determined for all standards and spiked samples (Table S1). Analyte
285 identity in unknown samples was confirmed when the quantitation/confirmation ion
286 ratios were within ± 1.96 standard deviations of the ratio determined for the standards
287 and spiked samples.

288 Procedural blanks, consisting of all steps in the extraction procedure except the
289 addition of soil, were run along with the unknown samples and standards to monitor for
290 potential contamination in reagents and sample processing. Procedural blanks were
291 always significantly below the lowest point on the standard curve (LOQ). In addition,
292 solvent blanks were run after every tenth sample to ensure that there was no carryover
293 between samples.

294

295 # 3. Results

296 ## 3.1 Spike Recovery

297 Recovery was determined by subtracting endogenous PFC levels from the
298 corresponding spiked samples (Table S2). Average percent recovery ± (SD) for all of the
299 PFCs was 98.6 ± (4.9) %, ranging from 75.5% for C14 to 120% for C12 for individual
300 recoveries.

301 ## 3.2 QC Soil

302 The QC soil sample was analyzed in duplicate with every batch of unknown soils
303 and to establish target values prior to analysis. Replicate analysis of this QC pool showed

the following 5 PFCs were found in the soil above the LOQ (~0.5 ng/g soil): C10 (0.69 ± 0.12 ng/g), C8 (3.76 ± 0.18 ng/g), C7 (7.75 ± 0.40 ng/g), C6 (1.70 ± 0.18 ng/g), and PFOS (2.38 ± 0.38 ng/g). The method showed good internal consistency over time with acceptable precision (average CV < 17.5%; Table S4).

**3.3 Replicate Analysis**

Ten percent of the analyzed soils (n = 6; one from every nation) were analyzed in duplicate for endogenous PFCs. PFCs concentrations were low in these six randomly selected soils, with three of the soils indicating no PFCs above the LOQ in both replicates. The remaining three soils had C6, C7, C8 and PFOS detectable at a concentration range of (1.42± 0.25 ng/g C8) to (6.17± 0.20 ng/g C7), with an average coefficient of variation of 14.4% for replicate analysis. C6 was detected in one sample (2.67± 0.37 ng/g, CV = 14.0%) and PFOS in 2 samples (1.64± 0.41 ng/g, average CV = 24.5%).

**3.4 Concentrations of PFCs in soils analyzed**

Thirteen individual PFCs were analyzed in these 60 soils with concentrations ranging from below the LOQ of ~0.5 ng/g dry weight soil to a high of 79.1 ng/g for the C7 acid (Table 1). The most commonly detected PFCs were PFOS>C8>C12>C7>C6. PFOS was measured above the LOQ in 48% of the samples, with a maximum concentration of 10.1 ng/g. The next most common compound was PFOA (C8) measured above the LOQ in 28% of the samples with a high of 31.7 ng/g. The C12 acid was quantifiable in 18% of the samples with a high of 3.94 ng/g, and the C7 acid was observed in 17% of the samples with a high of 79.1 ng/g. The median concentrations of

PFOS and PFOA were below the LOQ (not calculated for other PFCs), indicating typical left censored distributions common for most environmental data. None of the soils had concentrations of PFDS or PFBS above the LOQ but all of the other PFCs were detected in at least one soil above the LOQ. Table S3 shows summary statistics for the samples analyzed.

There was at least one PFC detected above the LOQ in 58.3% of the soil samples. The soils originating from the United States had quantifiable concentrations of PFCs in every sample (10/10) while only one of the ten soils from China had (1/10) quantifiable levels of PFCs. On a national basis, the number of soils (max n=10) with quantifiable concentrations of PFCs were: USA (10)> Mexico (9)> Japan (7)> Norway (6)> Greece (2)> China (1). Table 1 summarizes results from the ten highest soil sample concentrations determined in this study.

## 4. Discussion

While other methods for the analysis of PFCs in surface soils exist (Davis et al., 2007; Washington et al., 2007) this effort appears to be the first to assess standard addition recovery, replicate sample analysis, and analysis of a pooled QC soil using the same method. Though this method shows good accuracy and precision, the presence of PFCs in soils at these levels indicates the need for the development of a standard reference material (SRM) with appreciable PFC content to demonstrate comparability between methods. This method appears to perform well over presumed ranges of chemical and physical characteristics represented in these soils, and over a wide range of

perfluorinated compound chain lengths. Despite the complexity of soil as a matrix, this method is fairly straightforward.

Despite the increasing body of literature concerning the presence of the PFCs in environmental and biological media, very little research has been done with soil. This is a serious shortcoming given the central role that soil plays in water and air quality, food production, waste disposal, and other factors that are critical to environmental quality and human health. The lack of research may in part be due to the fact that, on a global scale, soils are quite heterogeneous, differing widely in their chemical and physical characteristics, making it difficult to establish reliable methods with broad applicability. To address this pressing need we have developed a fundamental method and applied it to 60 soils collected from 6 countries to assess it performance characteristics and to begin to evaluate what might be considered global "background" levels of the PFCs. Surface soils appear to be an environmental compartment to consider as an important reservoir.

The documented presence of large amounts of PFCs in atmosphere (Ellis et al., 2004; Stock et al., 2004; Kim and Kannan, 2007; Stock et al., 2007) and their movement via wind and weather systems is frequently suggested as a principal mechanism by which these materials are distributed in the environment. Materials that are present in the air are brought back to earth via rain or dry particle deposition where they go directly in to water systems or soils on the land (Liu et al., 2009). These atmospheric processes are likely to be heterogeneous, with variation associated with local inputs, precipitation patterns, and seasonal factors potentially contributing to this regional variability. The variation in PFC content in soils documented in this study is consistent with this hypothesis, suggesting

372 that large scale regional differences in soil concentration may play a role in
373 corresponding human exposures which may also occur on this same regional scale.
374
375 Considering this, it is interesting to note that all of the US soils evaluated in this
376 study had measureable levels of the PFCs, while soils from some of the other countries
377 had very little or no measureable PFCs. It may be that the generally higher levels of
378 PFCs in blood of US residents (Kannan et al., 2004) in comparison to the much of the
379 rest of the world are related to a greater exposure to PFCs in that country. This pattern
380 appears to be reflected in the US soils. Indeed, higher concentrations of PFCs have been
381 observed in environmental and biological matrices collected from the northern
382 hemisphere in comparison to materials from the southern hemisphere (Calafat et al.,
383 2006; Quinete et al., 2009). This difference has been attributed to more wide spread
384 industrialization in the north and relatively distinct air and ocean masses in these two
385 regions of the world. Given the relative ease with which soil samples can be collected
386 and analyzed, much more evaluation of broad scale regional patterns is clearly warranted.
387
388 The direct sources of PFCs discussed above show how soil can play a central role
389 in the accumulation and distribution of these materials in the environment, making it
390 clear that analysis of soils is important in helping to assess the extent of contamination
391 and potential for human exposure. But the findings from the current study also suggest
392 more subtle widespread regional contamination patterns may occur, and that evaluation
393 of this information is useful. While the data from the current study may not be
394 representative of conditions worldwide, we can use them to begin to make an estimate of

395 the PFC storage potential for the global soil compartment. Figure 1 is a log linear plot of
396 all of the PFOA and PFOS data ≥LOQ collected in this study, clearly indicating the
397 typical lognormal distributions that commonly occur with environmental contaminant
398 data. These data were used in a maximum likelihood procedure to estimate global
399 median concentrations of 0.124 ng/g for PFOA and 0.472 ng/g for PFOS (Table S3).
400
401 To help assess the potential validity of these estimates, we can apply them as
402 follows. Typically the most biologically active and important soil layer is the top 15 cm
403 (6 inches). A hectare furrow slice (HFS) of soil (~ 15 cm deep x 100 m x 100 m) with a
404 bulk density of 1.0-1.6 g/cm$^3$ has a mass of approximately 2.2 x 10$^6$ kg of soil (Brady,
405 1990). With the median value of 0.124 ng/g for PFOA determined in this study, a HFS
406 would have approximately 0.273 g PFOA. Given that the earth's land area is
407 150,000,000 km$^2$ (1.5 x 10$^{10}$ hectares) and assuming PFOA is only contained in the top
408 15cm of soil, we can further calculate 1,860 metric tons (MT) of PFOA globally
409 distributed in surface soils. When compared to a recent estimation of the total worldwide
410 production of PFO/APFO at 3,600 – 5,700 MT made by Prevedouros et al., 2006 (19), we
411 see that this estimated total soil loading is approximately 33% of the calculated maximum
412 production value. Of course the total world PFOA is partitioned into atmospheric,
413 oceanic, and earth surface (soil) sinks, and the relative proportion of each compartment is
414 in fact very difficult to determine. But general agreement of these new data with the
415 previous estimate of total production suggests that the global median value determined
416 above is plausible and that soils in general are likely be as important as the oceans and
417 the atmosphere.

In another previous study Armitage et al., 2006 (Armitage et al., 2006) estimate direct and indirect sources of perfluorooctanoate have been 2,723 – 5,935 MT, with 55% going to water, 31% to air, and 14% to land. The data from the current effort are again consistent with this determination, but our data suggest that soils are likely to be more important by a factor of approximately 2.

For PFOS, the calculated overall median concentration of 0.472 ng/g leads to approximately 1.04 g PFOS per HFS of soil, with a corresponding 7,080 MT of PFOS in global soils. Paul et al. have calculated that the between 1970 and 2002 approximately 122,500 MT of perfluorooctane sulfonyl fluoride (POFS) was produced (Paul et al., 2009), all of which could potentially degrade to PFOS. The current study's estimate of global soil loading is 6% of this total estimated production, which again is consistent with previous work and an indication that soil is likely to play an important role as a global sink.

One aspect of PFC soil contamination issue that is starting to receive considerable attention is the practice of disposing wastewater treatment (WWTP) plant effluents on soils. Biosolids in particular have often been considered to be a beneficial soil amendment due to residual levels of nutrients, but the PFC and other persistent pollutants are also often enriched in these effluents (Schultz et al., 2006; Loganathan et al., 2007). Disposal of these materials by application to cropland or "natural" areas is common in many parts of the world, and may lead to large scale contamination of soils, perhaps in a

441 manner that is similar to the situation documented in Germany that is discussed earlier
442 (Holzer et al., 2008; Wilhelm et al., 2008a; Wilhelm et al., 2008b). The USEPA estimates
443 that about 50% of all biosolids in the US are being recycled to land, including agricultural
444 areas (USEPA). Moreover, because the carboxylate and sulfonate PFCs are likely to
445 remain as anionic species at environmental pH, they will have some degree of mobility in
446 soils, which are also overwhelmingly negatively charged (Brady, 1990). This gives rise
447 to the possibility of subsequent migration of the PFCs to adjacent water supplies, uptake
448 by crops grown on these soils, and concentration in livestock grazing in these areas. At
449 this time at least two more cases of land application of PFC containing WWTP waste
450 have been documented in the US (Konwick et al., 2008; USEPA, 2009) , with the
451 analysis of soil providing the first indication of the nature and magnitude of the situation.
452 WWTP effluent applications in agricultural areas may warrant further investigation given
453 that research is beginning to show that that PFOS and PFOA are taken up from soil into
454 plants (Stahl et al., 2008), routing these materials directly into the human food chain.
455 None of these samples in this present study are from areas with known WWTP biosolids
456 application.
457
458 This work demonstrates a robust, sensitive method (low ng/g soil) that could be
459 used to gather more representative soil data. It is clear that much more research will be
460 needed before an accurate estimation of the global distribution of PFCs in surface soils
461 can be made. This research suggests soils should be investigated further as a global sink
462 for the PFCs, and as a source for potential environmental and human exposures. Broad
463 scale application of the method presented in this work will provide refined data on the

global distributions of the PFCs and should help identify both regional trends and "hotspot" areas where significant contamination has occurred. Intensive investigation of areas which have received application of effluents from WWTPs would be helpful to help evaluate potential impacts to soil, water, food, and human populations. With minor modifications this method has been applied successfully to investigate soils in Decatur, AL with significantly higher PFC concentrations (Washington et al., 2009). The method described here will allow for the examination of PFCs in surface soils at low levels of detection (ng/g) with adequate precision and accuracy to answer questions about PFC accumulation related to local and distant sources, potential motility to water resources, uptake by plants, and ultimately global fate and transport.

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*This document is a preliminary draft. It has not been formally released by the United States Environmental Protection Agency and should not at this stage be construed to represent Agency policy. It is being circulated for comments on its technical merit and policy implications.*

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**Supplementary Material Available**

Additional method description, tables showing UPLC-MS/MS conditions, mass transitions of each analyte, and data on method performance are available in supplementary material.

**Table**

**Click here to download Table: Table 1.doc**

Table 1. Measured concentrations (ng/g) in the ten soils with the highest total concentrations of PFCs.

| Sample | description | C14 | C13 | C12 | C11 | C10 | C9 | C8 | C7 | C6 | PFDS | PFOS | PFHS | PFBS | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| NC04 | RTP, NC (USA) | --- | --- | --- | --- | 2.03 | 0.609 | 31.7 | 79.1 | 12.4 | --- | 2.55 | 0.527 | --- | 129 |
| NC02 | RTP, NC (USA) | --- | --- | --- | --- | 0.958 | --- | 15.6 | 34.1 | 5.36 | --- | 0.606 | --- | --- | 56.6 |
| NC05 | Shinning Rock, NC (USA) | --- | --- | 1.85 | --- | 0.845 | --- | 8.40 | 19.8 | 5.62 | --- | 1.47 | --- | --- | 37.9 |
| J28-3 | Osaka (Japan) | 4.01 | 2.24 | 3.94 | 1.31 | 1.88 | --- | 21.5 | --- | --- | --- | 0.584 | --- | --- | 35.5 |
| TX03 | Houston, TX (USA) | --- | --- | --- | --- | --- | --- | 2.66 | 6.12 | 2.96 | --- | 2.16 | --- | --- | 13.9 |
| KY01 | Richmond, KY (USA) | --- | --- | 1.73 | --- | --- | --- | 2.14 | 4.61 | 1.71 | --- | 1.60 | --- | --- | 11.8 |
| IN01 | W. Layfayette, IN (USA) | --- | --- | 1.02 | 1.10 | 0.560 | --- | 2.18 | 3.52 | 1.51 | --- | --- | 1.39 | --- | 11.3 |
| M2 | Mexico City (Mexico) | --- | --- | --- | --- | --- | --- | 0.764 | --- | --- | --- | 10.1 | --- | --- | 10.8 |
| J1-2 | Hokkaido (Japan) | --- | --- | 2.38 | --- | --- | --- | 1.84 | | | --- | 5.15 | --- | --- | 9.37 |
| NC07 | Laurel Fork, NC (USA) | --- | --- | 1.44 | --- | --- | --- | 1.35 | 1.56 | 0.945 | --- | 2.52 | --- | --- | 7.81 |

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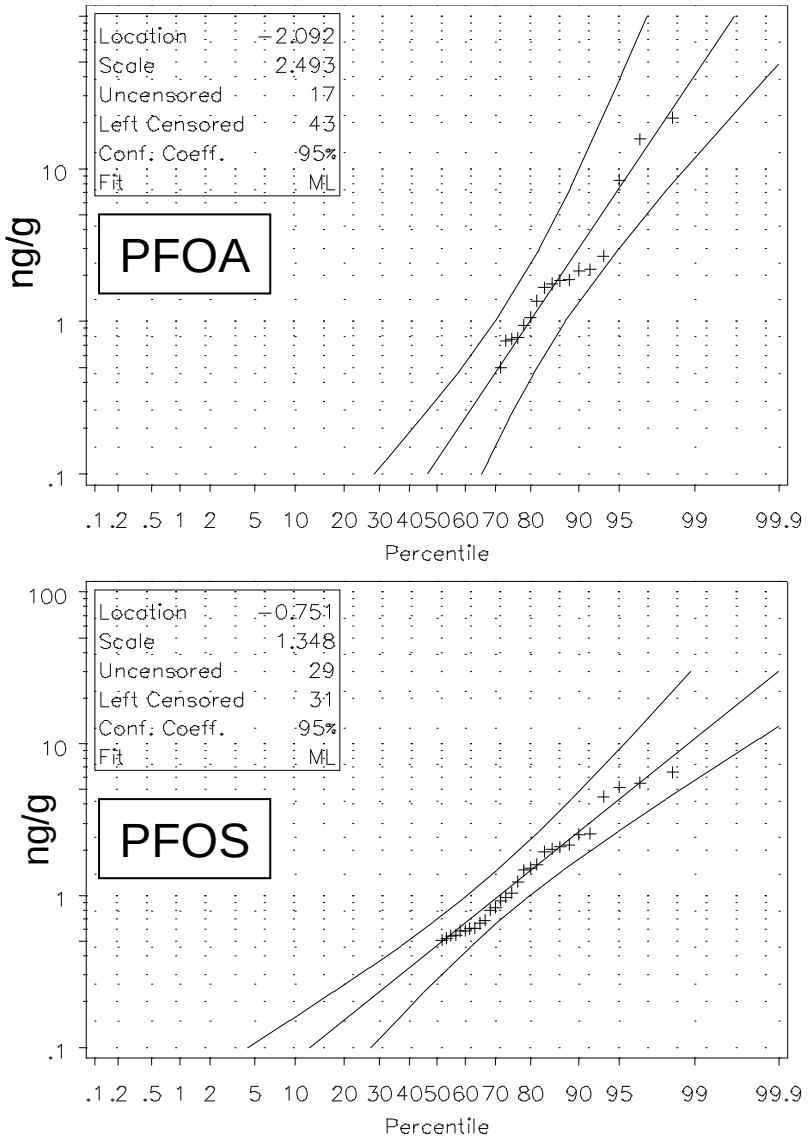
Figure 1.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Percentile

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